ARCHIVES OF ACOUSTICS
21, 4, 431–446 (1996)

ULTRASONIC INVESTIGATIONS OF INCLUSION COMPLEXES OF α-CYCLODEXTRIN WITH SODIUM ALKYL SULFATES. KINETIC AND THERMODYNAMIC PARAMETERS

A. JUSZKIEWICZ

Department of Chemistry
Jagiellonian University
(30-060 Kraków, ul. Ingardena 3)

A. BALCERZAK

Institute of Fundamental Technological Research
Polish Academy of Sciences
(00-049 Warszawa, Świętokrzyska 21)

Velocity and attenuation measurements of ultrasonic waves in aqueous solutions of α-cyclodextrin containing different sodium alkyl sulfates were made. The occurrence of an ultrasonic relaxation process, most probably connected with a deeper penetration of the alkyl chain into the cyclodextrin cavity and a more tight structure of the inclusion complexes of α-cyclodextrin with sodium decyl-, dodecyl- and tetradecyl sulfates, has been established. Thermodynamic and kinetic parameters related to this process have been calculated.

1. Introduction

Cyclodextrins (CD) are known to form so-called inclusion compounds by capturing a number of compounds into their cavities. CD are cyclic carbohydrates consisting of six (α-CD), seven (β-CD), or eight (γ-CD) D–(+) – glucopyranose units linked by α– (1.4) interglucose bonds. CD has a unique spatial configuration forming a torus shaped molecular structure with a hydrophilic exterior and a hydrophobic interior. The hydrophobic cavity forms an ideal harbor in which poorly water-soluble molecules can shelter their most hydrophobic parts. The contact between such a poorly soluble compound and CD in aqueous enviroment can result in complexation in that no covalent bonds are formed. Due to the hydrophilic outside of the CD, such a complex is a soluble entity on its own. Thus, the CD has been well-known to form inclusion compounds with a variety of molecular species by several kinds of driving forces [1, 2], where the hydrophobic interaction has been found to play an important role [2-6].

Inclusion of organic compounds by CD sometimes inhibits oxidation or biological digestion of the included compounds. The inclusion complexes have been, therefore, widely used in the fields of food, drug and agricultural industries as an encapsulating agent to protect sensitive molecules in hostile environments. CS also show catalytic activities in many kinds of reactions such as hydrolysis, decarboxylation, hydrogenation of olefins, site-specific substitution reactions of included compounds, and so on. Thus it would be of special interest to determine the fundamental processes at work when the cyclodextrin play host to other molecules in the solution.

It has been demonstrated that the addition of CD to an aqueous solution of a surfactant affects dramatically the physicochemical properties of the solution [7-32]. The reason for these changes is the ability of CD to screen the hydrophobic moieties of the surfactant molecules from contact with the surrounding aqueous media by the formation of an inclusion complex in which the hydrophobic chain of the sufractant is inserted into the CD cavity. As a result, surfactants are ideal guests which allow a systematic study of complexation with cyclodextrins since both their hydrophobic and hydrophilic (with different degree of hydrophobicity) moieties can be systematically changed. Indeed, the ability of cyclodextrins to modify the physicochemical properties of such aqueous solutions has been used to study their complexation behavior with surfactants, and a variety of experimental techniques have been used for this purpose. They include conductivity [10-16], competitive bindind using UV – visible and fluorescent probes [16-21], NMR [22], surface tension [23], sound velocity [24-28] ultrasound absorption [29, 30] and electrochemical [24, 31, 32] methods.

The ultrasonic spectroscopy technique is an important tool for the elucidation of basic solution processes and reaction mechanisms occurring in the microsecond to nanosecond range. Despite of the kinetic information, ultrasonic relaxation studies can provide thermodynamic information about the relaxation process [29, 30, 33, 34]). One such area still not well understood is the inclusion of guest molecules by cyclodextrins in their cavities.

In this article the results of the ultrasonic investigation of the inclusion complexes of α-cyclodextrin (α-CD) with sodium alkyl sulfates C_nH_{2n+1} OSO_3Na (n = 6, 8, 10, 12, 14) are presented.

2. Experimental part

Measurements of the ultrasonic velocity and the attenuation coefficient α/f^2, in the aqueous solutions of the α-CD with the sodium alkyl sulfates C_nH_{2n+1} OSO_3 (n = 6, 8, 10, 12, 14) were performed in the frequency range 1-150 MHz at 15, 25, 35 and 45°C and the concentration of 0.04M of each of the component. At 25° the measurements were also made for 0.01, 0.02 and 0.03 M equimolar solutions.

The measurements were made by means of the resonator [35-37] and pulse [34, 38] methods in the frequency range 1-10 MHz and 10-150 MHz, respectively. The measurement errors were about 5% for the former method and below 1% for the

latter one. Detailed descriptions of the equipments used in the resonator and pulse methods are presented in [36, 37] and [38, 39], respectively.

The theoretical curves were fitted to the experimental results by means of computer calculation programs. Those curves are given by the well known theoretical equation

$$\mu = 2\sum_{i=1}^{n} \mu_{m_i} \frac{f/fr_i}{1 + (f/fr_i)^2}, \tag{2.1}$$

where f is the measured frequency, fr_i the relaxation frequency, $\mu = (\alpha - Bf^2)\lambda$ represents the excess attenuation wavelength ($\lambda = c/f$, c is the ultrasonic velocity), α is the ultrasonic attenuation, B is the contribution to sound attenuation from any other processes that may occur at higher frequencies beyond the frequency range measured, μ_{m_i} is the maximum excess attenuation per wavelength, n is the number of relaxation processes.

3. Results and discussion

Results of the measurements are presented in Table 1 and Figs. 1, 2.

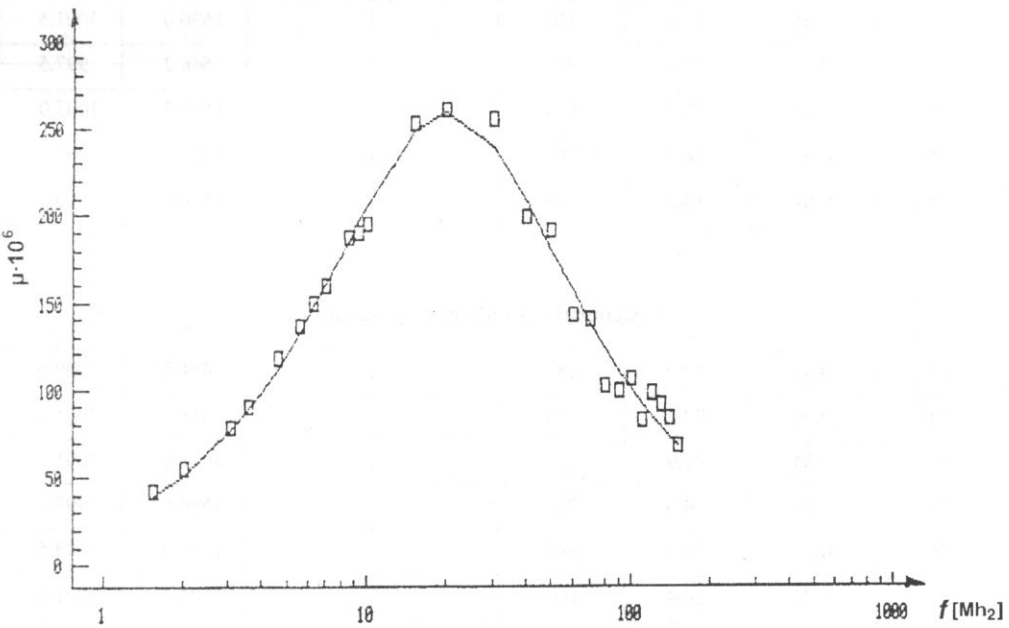

Fig. 1. Representative plot of the excess sound attenuation per wavelength, μ, vs. frequency, f, for the aqueous solution of α-CD and sodium octyl sulfate. Temperature 25°C, concentration $C = 0.04$M.

Table 1. Ultrasonic relaxation parameters, sound velocities and densities at various temperatures and concentrations for the aqueous solutions of α-cyclodextrin with sodium alkyl sulfates.

t [°C]	C [M]	f_{r1} [MHz]	$\mu_{m1} \times 10^6$	f_{r2} [MHz]	$\mu_{m2} \times 10^6$	c [m/s]	ρ [kg/m^3]
			α-cyclodextrin				
15	0.04	15.9	264			1478.2	1009.0
25	0.04	16.7	234			1506.0	1004.9
35	0.04	18.8	204			1528.9	1001.2
45	0.04	19.6	189			1543.4	997.0
25	0.03	16.8	172			1503.6	1003.1
25	0.02	16.7	102			1501.4	1001.0
25	0.01	16.4	68.2			1499.1	999.0
			α-cyclodextrin + sodium hexyl sulfate				
15	0.04	18.0	284			1480.1	1009.3
25	0.04	18.9	250			1510.0	1005.3
35	0.04	20.6	210			1530.0	1001.5
45	0.04	22.1	203			1546.2	997.5
25	0.03	18.8	175			1506.7	1003.0
25	0.02	18.5	103			1503.3	1001.2
25	0.01	19.2	69.3			1500.1	999.1
			α-cyclodextrin + sodium octyl sulfate				
15	0.04	19.5	287			1481.2	1009.6
25	0.04	20.2	259			1511.7	1005.6
35	0.04	21.9	233			1531.6	1001.7
45	0.04	24.0	203			1550.5	997.7
25	0.03	20.5	193			1508.0	1003.5
25	0.02	20.4	109			1504.3	1001.6
25	0.01	20.3	70.5			1500.4	999.2

Table 1 [cont.]

α-cyclodextrin + sodium decyl sulfate

15	0.04	24.7	293	5.4	778.3	1480.3	1010.8
25	0.04	25.8	263	6.3	85.6	1511.87	1007.0
35	0.04	28.1	240	8.8	96.8	1530.5	1003.0
45	0.04	29.9	205	9.9	106	1549.4	999.1
25	0.03	26.0	206	5.9	71.5	1508.1	1004.5
25	0.02	25.8	120	6.4	38.4	1504.3	1001.9
25	0.01	25.3	70.7	6.2	20.1	1500.5	999.6

α-cyclodextrin + sodium dodecyl sulfate

15	0.04	32.1	319	7.0	157.3	1481.9	1012.7
25	0.04	33.6	283	8.0	181	1512.1	1008.9
35	0.04	36.1	261	9.4	210	1531.9	1004.7
45	0.04	38.0	222	11.2	225	1550.8	1000.8
25	0.03	33.8	227	7.8	129	1508.1	1005.7
25	0.02	33.9	128	8.0	105	1504.4	1002.5
25	0.01	33.4	77.2	7.9	53.1	1500.6	1000.0

α-cyclodextrin + sodium tetradecyl sulfate

15	0.04	34.1	336	7.6	216.3	1482.1	1013.6
25	0.04	35.7	290	8.9	247	1513.0	1009.8
35	0.04	38.3	254	9.6	278	1533.0	1005.7
45	0.04	39.9	234	10.9	333	1551.8	1001.8
25	0.03	35.3	228	9.3	168	1509.1	1006.6
25	0.02	36.0	144	9.0	112	1504.8	1003.4
25	0.01	36.1	83.1	8.6	64.5	1500.8	1000.3

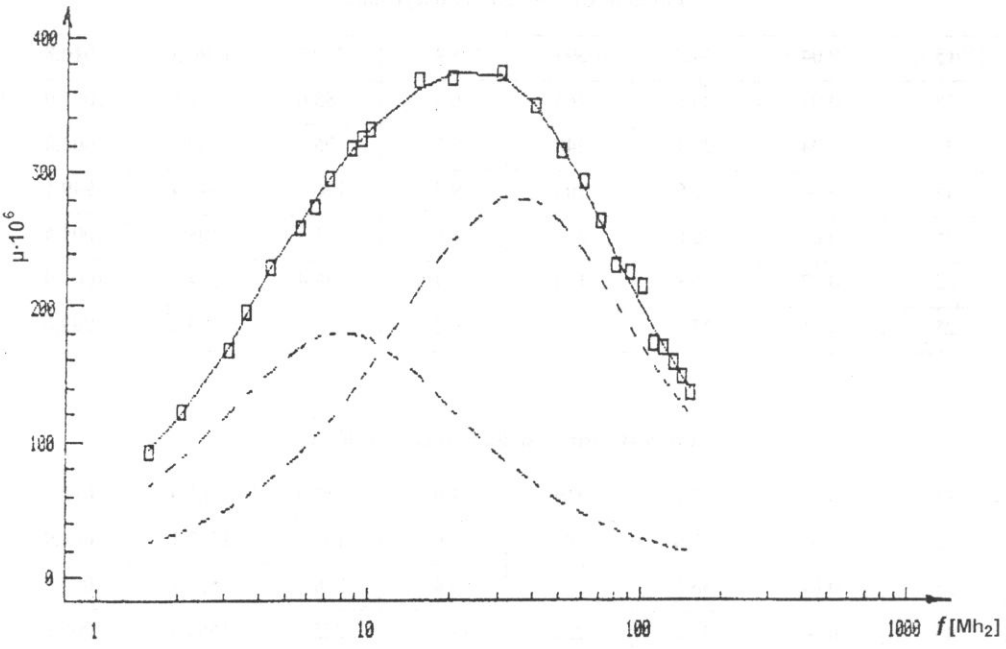

Fig. 2. Representative plot of the excess sound attenuation per wavelength, μ, vs. frequency, f, for the aqueous solution of α-CD and sodium dodecyl sulfate. Temperature 25°C, concentration $C = 0.04$M.

As an result of the carried out measurements, the high frequency relaxation processes 18-33 MHz have been found in all the investigated aqueous solutions of α-CD and the surfactants. The ultrasonic, kinetic and thermodynamic parameters of these processes are similar to those for the aqueous solution of α-CD without surfactants [39]. These relaxation processes are caused by the water molecule exchange in the hydratation shell of the α-CD molecule [29, 40]. Thus one can conclude that this kind of exchange is only slightly modified by the surfactant accomodated in the cavity of CD. More information about that will be published in another work.

In aqueous solutions of sodium decyl-, dodecyl- and tetradecylsulfate with α-CD, additional low-frequency relaxation processes were found. Within the limits of the experimental error ($\cong \pm 5\%$), for all these processes there is no dependence of the relaxation frequency f_r on the concentration of the solution C within the investigated f_r and C ranges. A linear dependence of the maximum excess attenuation per wavelength μ_m, on the concentration C has been found. Both these experimental facts indicate that the origin of these low-frequency relaxation processes is a first-order or pseudo-first-order reaction, the equilibrium of which is disturbed by the propagating ultrasonic wave

$$A_1 \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} A_2, \tag{3.1}$$

where, in this case, A_1 and A_2 denote two stages of the inclusion complex, k_1 and k_{-1} are the rate constants for the direct and opposite reactions, respectively.

For this kind of reaction, the following kinetic and thermodynamic formulas can be derived [41-43].

The relaxation time τ^{-1} is given by

$$\tau^{-1} = 2\pi f_r = k_1 + k_{-1} = k_{-1}(1 + k) = \frac{kT}{h} \exp(\Delta S^*_{-1}/R) \exp(-\Delta H^*_{-1}/RT)\,(1 + K), \tag{3.2}$$

where $K = k_1/k_{-1}$ is the equilibrium constant for reaction (3.1) ΔS^*_{-1} and ΔH^*_1 are the activation entropy and activation enthalpy for the opposite reaction, respectively, T is the absolute temperature, R is the gas constant, k is the Boltzmann constant and h is the Planck constant.

The plot of the function (3.2) in $\ln(f_r/T)$ and $(1/T)$ coordinates is a straigth line with the slope

$$a_f = \frac{\Delta H^*_{-1}}{R} - \frac{K}{(1 + K)} \frac{\Delta H^0}{R}, \tag{3.3}$$

and the intercept b_f

$$b_f = \ln(k/2\pi h) + \frac{\Delta S^*_{-1}}{R} \tag{3.4}$$

if the following formula

$$\frac{d \ln(K)}{d\ (1/T)} = -\frac{\Delta H^0}{R} \tag{3.5}$$

has been applied. ΔH^0 is the enthalpy of the reaction (3.1).

The maximum excess attenuation per wavelength μ_m can be expressed as

$$\mu_m = \frac{\pi}{2\beta} \frac{\Delta V_s^2}{RT} ([A_1)^{-1} + [A_2]^{-1}) = \frac{\pi}{2\beta} \frac{\Delta V_s^2}{RT} \frac{K}{(1 + K)^2} C, \tag{3.6}$$

where β is the adiabatic compressibility, ΔV_s is the isentropic change of volume which accompanies the transition from the state A_1 to state A_2. $[A_1]$ and $[A_2]$ are the molar concentrations of molecules being in both the states, C is the total molar concentration, ΔV_s is related to ΔV_T, the isothermic change of volume, by the relation

$$\Delta V_s = \Delta V_T - \frac{\Theta}{\rho C_p} \Delta H^0, \tag{3.7}$$

where ρ denotes density, Θ is the expansivity and C_p is the specific heat under constant pressure. In the $\ln(\mu_m \beta T)$ and 1/T coordinates, the plot of equation (3.6) is a straigth line if the very weak temperature dependencies of ΔV and C are neglected. The slope a_μ of this line is equal to

$$a_\mu = \frac{\Delta H^0}{R} \frac{K-1}{K+1}. \tag{3.8}$$

The inercept b_μ is

$$b_\mu = \ln\left[\frac{\pi}{2} \frac{\Delta V_s^2}{R} C\right]. \tag{3.9}$$

In order to calculate the equilibrium constant K, equations (3.3) and (3.8) can be combined into the following one

$$\frac{f_r}{\frac{kT}{2\pi h}\exp(\Delta S^*_{-1}/R)} = \exp\left[\frac{1}{T}\left(a_f + \frac{K}{K-1} a_\mu\right)\right](1+K). \tag{3.10}$$

From the ultrasonic measurements one can determine a_f, a_μ and ΔS^*_{-1} (eq. (3.4)), and subsequently K.

Thus from the above mentioned dependencies, the values of the following parameters can be calculated: ΔS^*_{-1} (Eq. (3.4)), K (Eq. (3.10)), ΔH^0 (Eq. (3.8.)), ΔH_1 (Eq. (3.3)), k_{-1} (Eq. (3.2)). Next, from these values one can determine:

the rate constant of the direct reaction

$$k_1 = K k_{-1}, \tag{3.11}$$

the free enthalpy of activation of the opposite reaction ΔG^*_{-1},

$$\Delta G^*_{-1} = \Delta H^*_{-1} - T\Delta S^*_{-1}, \tag{3.12}$$

the free enthalpy of activation of the reaction (3.3), ΔG^0,

$$\Delta G^0 = -RT \ln K, \tag{3.13}$$

the entropy of this reactions, ΔS^0,

$$\Delta S^0 = \frac{\Delta H^0 \Delta G^0}{T}, \tag{3.14}$$

the enthalpy of activation of the direct reaction, ΔH^*_1,

$$\Delta H^*_1 = \Delta H^0 + \Delta H^*_{-1}, \tag{3.15}$$

the entropy of activation of this reaction, ΔS^*_1,

$$\Delta S^*_1 = \Delta S^0 + \Delta S^*_{-1}, \tag{3.16}$$

and the free enthalpy of a activation of the direct reaction, ΔG^*_1,

$$\Delta G^*_{1} = \Delta G^0 + \Delta G^*_{-1}. \tag{3.17}$$

The modulus of the molar volume change which accompanies reaction (3.1) $|\Delta V_s|$ could be obtained by transforming Eq. (3.9)

$$|\Delta V_s| = \left[\frac{2R}{\pi}\frac{1}{C}\exp b_\mu\right]^{\frac{1}{2}} \tag{3.18}$$

However, the error of this value is usually significant. Eq. (3.18) contains an exponential function which exponent b_μ is not too reliable because of the long extrapolation required. $|V_s|$ can be determined more precisely from Eq. (3.19), which results from the transformation of Eq. (3.6)

$$|V_s| = \left[\frac{2RT\beta}{\pi}\frac{(1+K^2)}{K}\frac{\mu_m}{C}\right]^{\frac{1}{2}} \tag{3.19}$$

In this case, as one can notice, it is necessary to measure the ultrasonic absorption for different values of C to determine the ratio μ_m/C.

For the tested solutions of α-CD and a surfactant, the kinetic and thermodynamic parameters of the low-frequency relaxation process, calculated from the above formulas, are presented in Table 2 and Figs. 3-11.

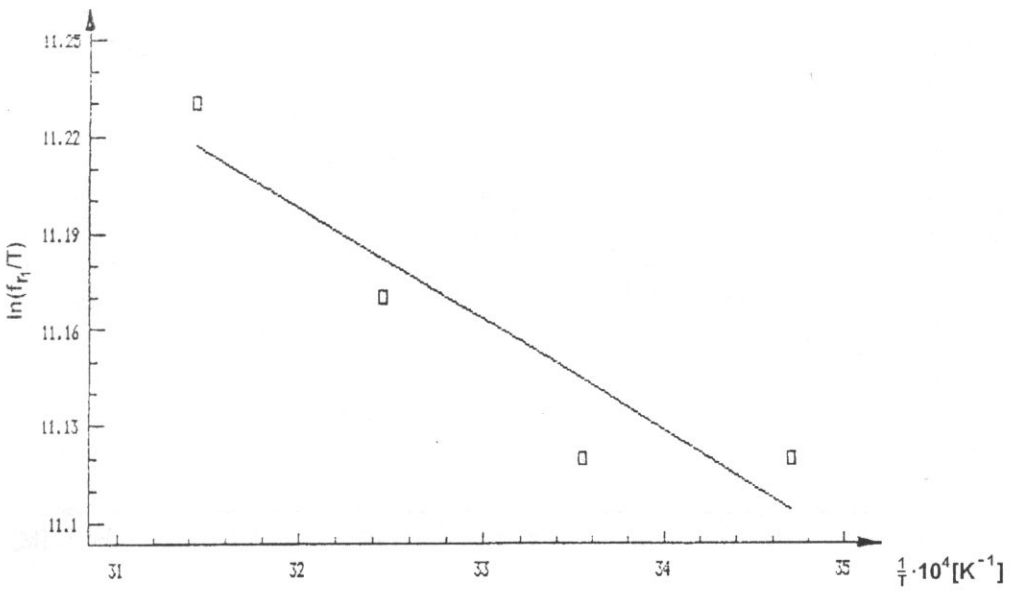

Fig. 3. Plot of μ_{m1} vs. C for the aqueous solution of α-CD and sodium octyl sulfate. Temperature 25°C.

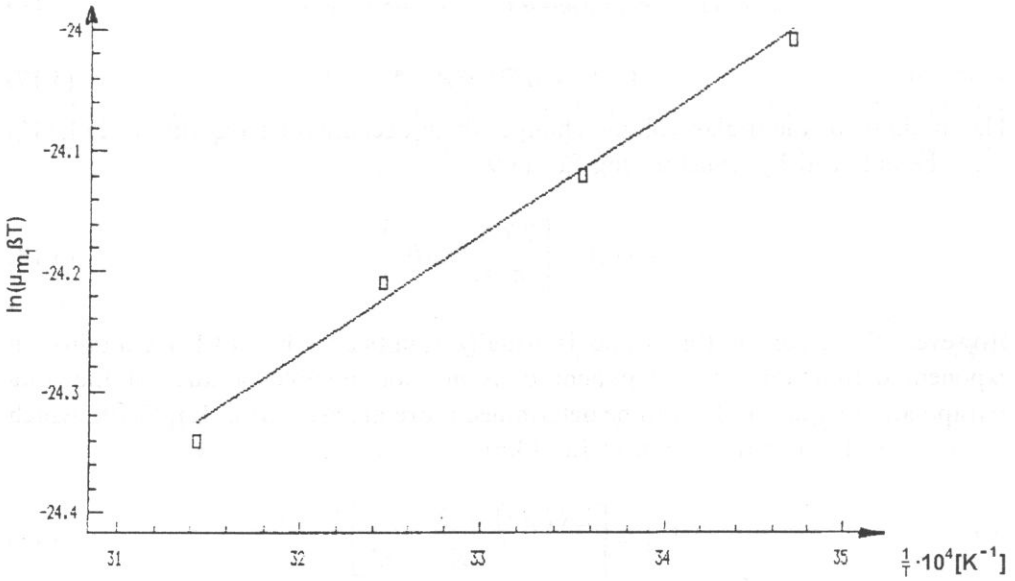

Fig. 4. Plot of $\ln(f_{rl}/T)$ vs. $(1/T)$ for the aqueous solution of α-CD and sodium octyl sulfate. $C = 0.04$ M.

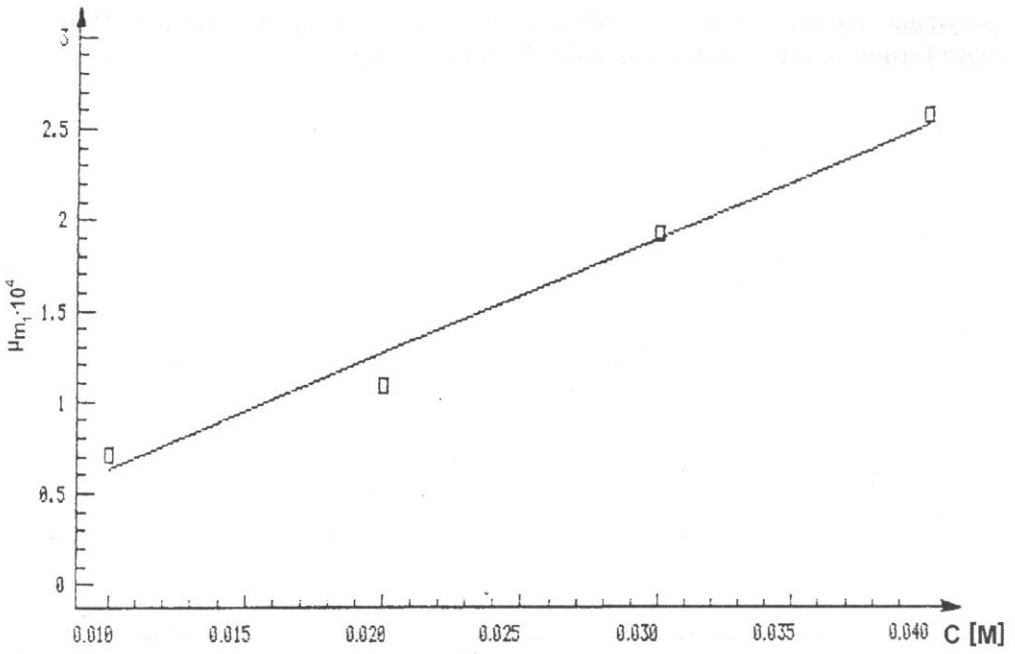

Fig. 5. Plot of $\ln(\mu_{m1}\beta T)$ vs. $(1/T)$ for the aqueous solution of α-CD and sodium octyl sulfate. $C = 0.04$ M.

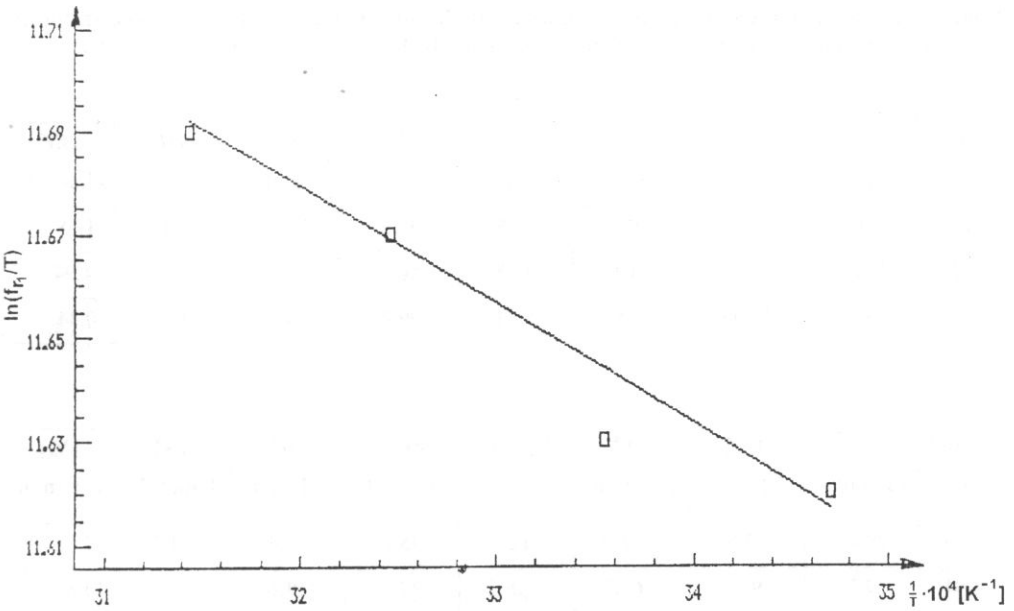

Fig. 6. Plot of μ_{m1} vs. C for the aqueous solution of α-CD and sodium dodecyl sulfate.Temperature 25°C.

The results obtained suggest that the investigated relaxation process is due to the penetration of the hydrophobic alkyl chain of the surfactant into the cavity of α-CD, this being connected with the rearrangement of the inclûsion complex into a more tight structure. The hydrophobicity of the alkyl chain increases with the length of its chain. This allows for a deeper penetration of the surfactant chain into the hydrophobic cavity of CD. This fact is confirmed by the observed increases of both the rate constant k and the equilibrium constant K when the value of n increases. The latter being rearranged into a more tight structure with a deeper built-in surfactant molecule. This complex makes CD + surfactant association more stable when the alkyl chain becomes longer. No low-frequency relaxation processes are observed for sodium hexyl sulfate and sodium octyl sulfate. This means that the above described complex does not occur in solution containing these surfactants. This is due to the lower hydrophobicity of the shorter alkyl chains of these surfactants which does not allow this chain to penetrate into the CD's cavity. Thus, the stability of this kind of association is very low.

There are several kinds of interactions between CD and the guest molecule: hydrophobic interaction, polar interaction, steric interaction, hydrogen bonding,

Table 2. Kinetic and thermodynamic parameters of the low-frequency relaxation process for the aqueous solutions of α-cyclodextrin with sodium alkyl sulfates $C_nH_{2n+1}OSO_3Na$ at 25°C.

n	a_f K^{-1}	b_f	a_μ K^{-1}	$\mu_m/C \cdot 10^6$ m^3/mol	K	ΔG^0 kJ/mol	ΔH^0 kJ/mol	ΔS^0 J/mol·K
10	-1706	15.73	-1007	2.18	30.2	-8.5	-9.0	-1.68
12	-1134	14.02	-1195	4.58	56.9	-10.3	-1.00	4.94
14	-762.3	12.83	-1352	5.94	99.4	-11.4	-11.5	-0.34

$k_1 \cdot 10^{-7}$ s^{-1}	ΔG^*_1 kJ/mol	ΔH^*_1 kJ/mol	ΔS^*_1 J/mol·K	$k_{-1} \cdot 10^{-5}$ s^{-1}	ΔG^*_{-1} kJ/mol	ΔH^*_{-1} kJ/mol	ΔS^*_1 J/mol·K	$\lvert V_s \rvert$ cm^3/mol
3.83	29.8	13.8	-53.2	12.7	38.2	22.8	-51.5	7.0
4.94	29.2	9.3	-66.7	8.7	39.2	19.6	-65.7	13.8
5.54	28.8	6.2	-75.9	5.6	40.2	17.7	-75.6	20.5

the torsional energy of the CD ring and the release of water molecules with high energies. Among these interactions, the hydrophobic and van der Waals (polar + steric) interactions might be mainly attributable to the thermodynamic parameters [44, 45].

The relatively very low value of ΔS^0 and its increase with increasing n can be caused by two competitive interactions. The increase of the length of the alkyl chain causes a decrease of the van der Waals interactions between a polar head of the surfactant and the hydroxyl groups at the edge of the CD molecule ($\Delta S < 0$). At the same time, the hydrophobic interactions of the more hydrophobic chain with the cavity increase ($\Delta S \geqslant 0$).

The decrease of ΔH^0, when n increases, can be attributed to the increase in the van der Waals interaction between the inner wall of the CD molecule and the alkyl chain of the surfactant.

Experimental data confirms the conclusions mentioned above.

The results of measurements obtained by means of different methods [10, 12, 16, 31, 46] indicate an increase in the stability constants of association of CD and the surfactants when the length of the carbon chain increases. The values of the stability constants are significantly greater than those of K. This indicates that K referes to one of the many steps that occurr in the complexation process [2].

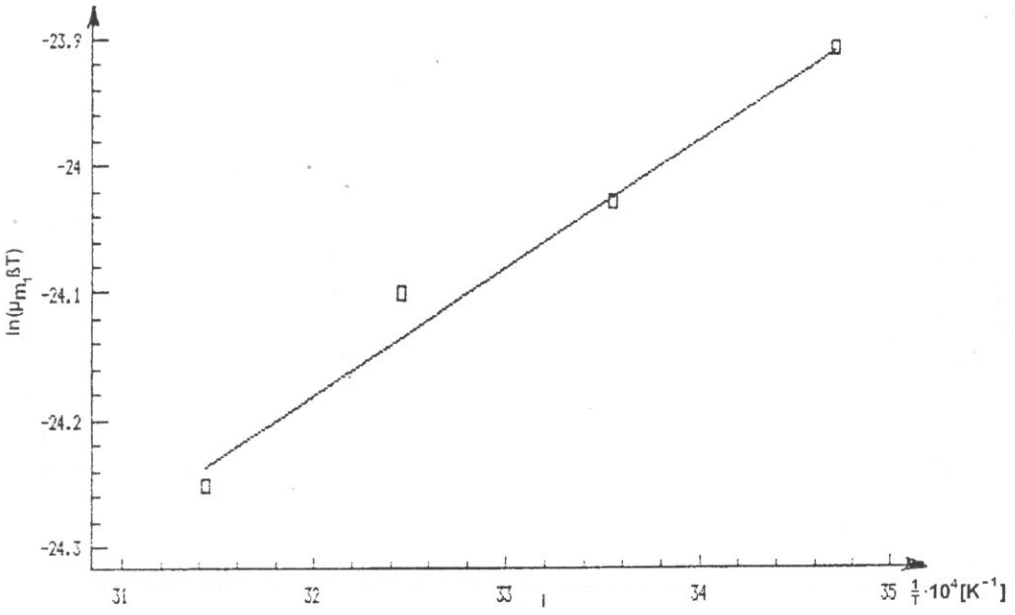

Fig. 7. Plot of μ_{m2} vs. C for the aqeous solution of α-CD and sodium dodecyl sulfate. Temperature 25°C.

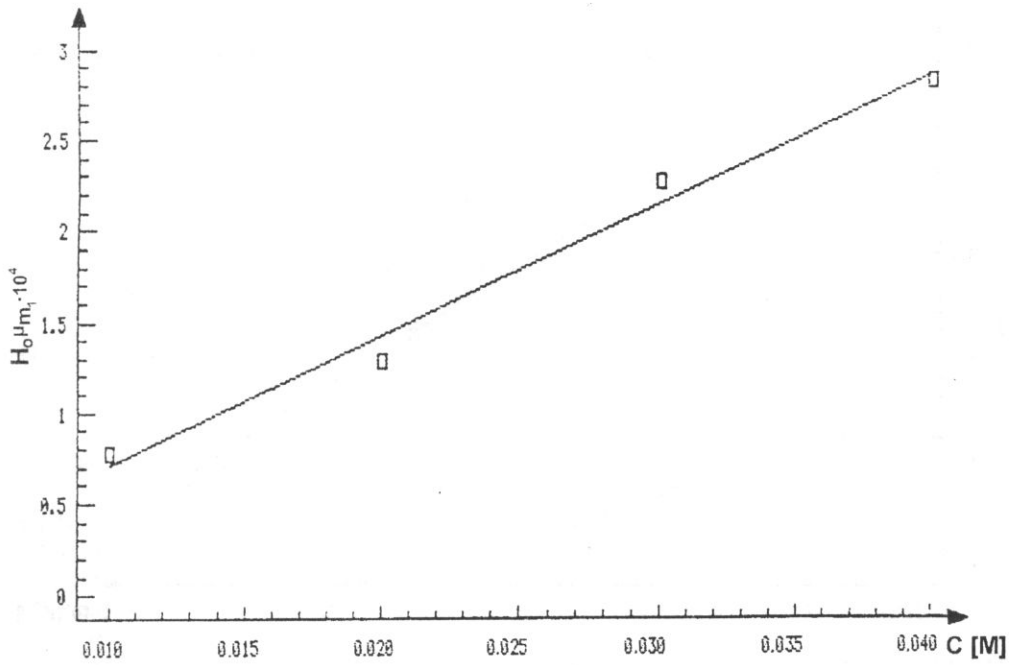

Fig. 8. Plot of $\ln(f_{r1}/T)$ vs. $(1/T)$ for the aqeous solution of α-CD and sodium dodecyl sulfate. $C = 0.04$ M.

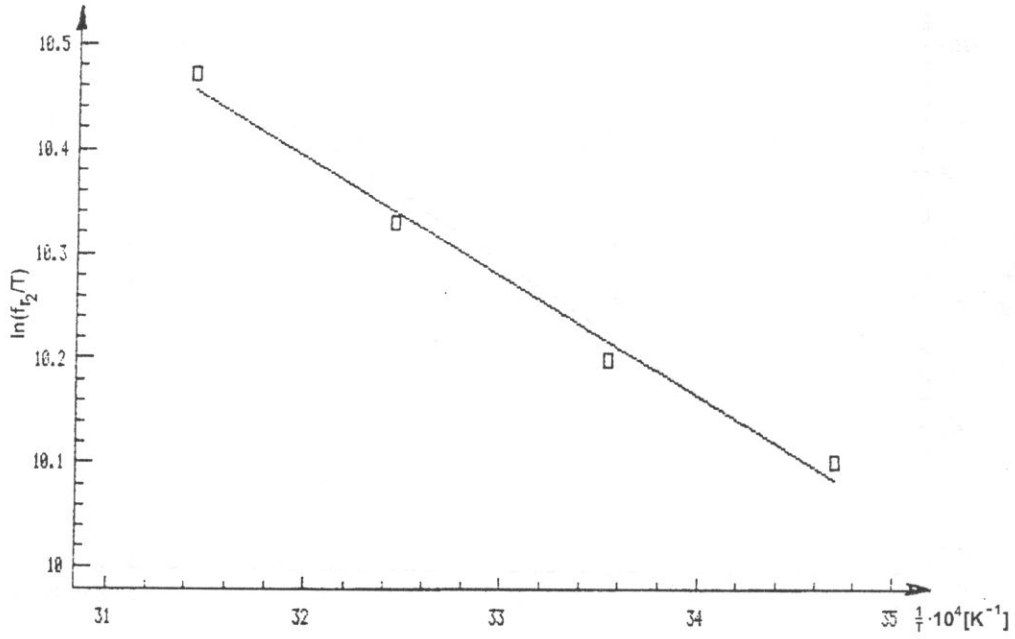

Fig. 9. Plot of $\ln(f_{r2}/T)$ vs. $(1/T)$ for the aqueous solution of α-CD and sodium dodecyl sulfate. $C = 0.04$ M.

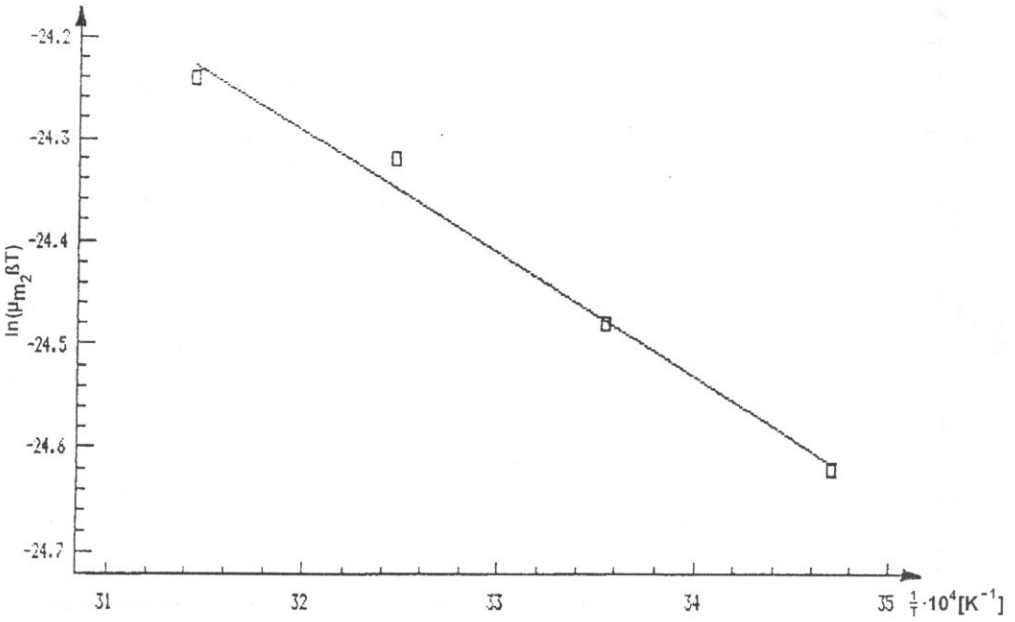

Fig. 10. Plot of $\ln(\mu_{m1}\beta T)$ vs. $(1/T)$ for the aqueous solution of α-CD and sodium dodecyl sulfate. $C = 0.04$M.

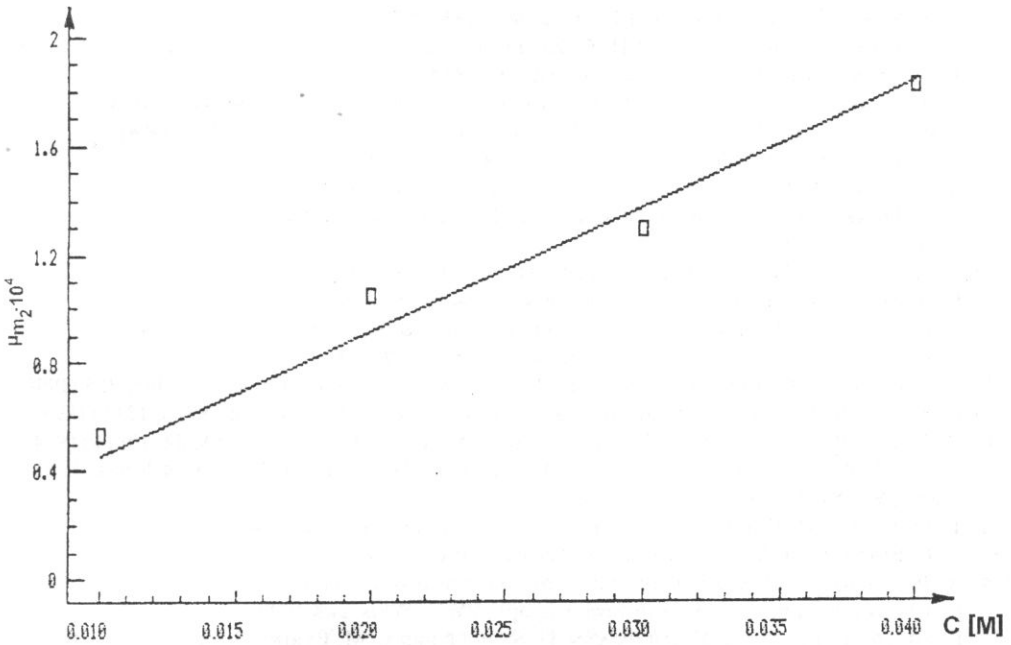

Fig. 11. Plot of $\ln(\mu_{m2}\,\beta T)$ vs. $(1/T)$ for the aqueous solution of α-CD and sodium dodecyl sulfate. $C = 0.04$ M.

References

[1] M. L. BENDER and M. KOMIYAMA, *Cyclodextrin chemistry*, Springer Verlag, Berlin 1978.
[2] J. SZEJTLI, *Cydlodextrins and their inclusion complexes*, Akademiai Kiado, Budapest 1982.
[3] M. KOMYIAMA and M. L. BENDER, J. Am. Chem. Soc., **100,** 2259 (1978).
[4] W SAENGER, Angew. Chem., **19,** 344 (1980).
[5] W. SAENGER, *Inclusion compunds*, (Eds.] J.L Atwood, J. E. D. Davies. D. D MacNicol. Academic Press, London 1984, vol. 2.
[6] C. TANFORD, *The hydrophobic effect. Formation of micelles and biological membranes*, 2 nd ed., John Wiley and Sons, New York 1980.
[7] T. OKUBO, H. KITANO and N.ISE, J. Phys. Chem., **80,** 2661 1976.
[8] N. FUNSSAKI, H.YODO and S. NEYA, Bull. Chem. Soc. Jpn., **65,** 1323 (1992).
[9] V. T. LIVERI, G. CAVALLARO, G. GIAMMONA, G. PITARRESI, G. PUGLISI and C. VENTUNA, Termochim. Acta, **199,** 125 (1992).
[10] I. SATAKE, T. IKENOUE, T. IAKESHITA, K. HAYAKAWA, T. MAEDA, Bull. Chem. Soc. Jpn., **58,** 2746 (1985).
[11] I. SATAKE, S. YOSHIDA, K. HAYAKAWA, T. MAEDA and Y. KOSUMOTO, Bull. Chem. Soc. Jpn., **59,** 3991 (1986).
[12] R. PALEPU and V. C. REINSBOROUGH, Can. J. Chem., **66,** 325 (1988).
[13] D. J. JOBE, R. E. VERRAL, R. PALEPU and V. C. REINSBOROUGH, J. Phys. Chem., **92,** 3582 (1988).
[14] R. PALEPU and V. C. REINSBOROUGH, Can. J. Chem., **67,** 1550 (1989).
[15] R. PALEPU, J. E. RICHARDSON, V. C. REINSBOROUGH, Langmuir, **5,** 218 (1989).

[16] E. S. AMAN, D. SERVE, J. Colloid Interface Sci., **183,** 365 (1990).
[17] A. HERSEY, B. H. ROBINSON and H. C. KELLY, J. Chem. Soc. Faraday Trans., I **82**, 1271 (1986).
[18] J. W. PARK and H. J. SONG, J. Phys. Chem., **93,** 6454 (1989).
[19] K. J. SASAKI, S. D. CRISTIAN, E. E. TUCKER, J. Colloid Interface Sci., **134,** 412 (1990).
[20] J. W. PARK, K. H. PARK, J. Inclusion Phenom. Mol. Recognit. Chem, **17,** 277 (1994).
[21] Y.-B. JIANG and X.-J WANG, Appl. spectrosc., **48,** 1428 (1994).
[22] B. M. FUNG, W. GUO, S. D. CHRISTIAN, Langmuir, 8, 446 (1992).
[23] U. R. DHARMAWARDANA, S. D. CHRISTIAN, E. E. TUCKER, R. W. TAYLOR, and J. F. SCAMEHORN, Langmuir, **9**, 2258 (1993).
[24] D. JEZEQUEL, A. MAYAFFRE, and P. LETELLIER, Can. J. Chem., **69,** 1865 (1991).
[25] E. JUNQUERA, E. AICART, and G. TARDAJOS, J. Phys. Chem., **96,** 4533 (1992).
[26] E. JUNQUERA, G. TARDAJOS and E. AICART, J. Colloid Interface Sci., **158,** 388 (1993).
[27] E. JUNQUERA, G. TARDAJOS and E. AIRCART, Langmuir, **9,** 1213 (1993).
[28] E. JUNQUERA, J. G. BENITO, L. PENA and E. AIRCART, J. Colloid Interface Sci., **163,** 355 (1994).
[29] D. J. JOBE, R. E. VERRALL, E. JUNQUERA and E. AIRCART, J. Phys. Chem., **97**, 6, 1243 (1993).
[30] D. J. JOBE, R. E. VERRALL, E. JUNQUERA and E. AICART, J. Phys. Chem., **98**, 42, 10814 (1994).
[31] W. M. Z. Wan YUNUS, J. TAYLOR, D. M. BLOOR, D. G. HALL and E. J. WYN-JONES, J. Phys. Chem., **96.**, 8979 (1992).
[32] T. TOMINAGA, D. HACHISU, and M. KAMADO, Langmuir, **10,** 4676 (1994).
[33] C. F. BERNASCONI, *Relaxation kinetics,* Academic Press, New York 1976.
[34] A. JUSZKIEWICZ and A. ANTOSIEWICZ, *Ultrasonic spectroscopy in molecular biophysics,* [in Polish] part II, vol. 5 [in monograph:] Biospectroscopy, PWN, Warszawa 1990.
[35] F. EGGERS, F. FUNCK, K. H. RICHMANN, H. SNEIDER and E. M. EYRING, J. Phys. Chem., **91**, 1961 (1987).
[36] G. GALIŃSKI, Z. KOZŁOWSKI, Sci. Instrum., **43,** 4 (1989).
[37] A. BALCERZAK, Z. BAZIOR, and Z. KOZŁOWSKI, [in Polish], IFTR Reports 17 (1992).
[38] A. BALCERZAK and R. PŁOWIEC [in Polish], IFTR Reports 21 (1994).
[39] A. JUSZKIEWICZ and A. BALCERZAK, Archives of Acoustics, **18,** 447 (1993).
[40] S. KATO, H. MOMURA and Y. MIYARA, J. Phys. Chem., **89,** 5417 (1985).
[41] J. LAMB, *Physical acoustics* , [Ed.] W. P. Mason, Academic Press, New York 1965, vol. II, part A, chapter 4.
[42] C. C. CHEN, S. PETRUCII, J. Phys. Chem., **86**, 2601 (1982).
[43] L. J. RODRIGUEZ, E. M. EYRING and S. PETRUCCI, J. Phys. Chem., **93,** 6356 (1989).
[44] S. J. GILL, N. F. NICHOLS and I. WADSO, J. Chem. Thermodyn., **8**, 445 (1976).
[45] P. D. ROSS and S. SUBRAMANIAN, Biochemistry, **20,** 3096 (1981).
[46] H. KITANO and T. OKUBO, J. Chem. Soc. Perkin Trans., **2,** 432 (1977).